ADAMANTANES FROM PETROLEUM, WITH ZEOLITES

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ABSTRACT

Circumstances have been found under which adamantanes are significantly concentrated and, it is believed, formed in a petroleum refinery, and catalysts have been identified which are effective in recovering these compounds from a complex mixture of similarly boiling hydrocarbons. In an example detailed below, nearly 10% adamantanes, largely methyl-substituted derivatives, were found in and isolated from a refinery stream by selectively removing the non-adamantanes with a Pt-containing zeolite Beta catalyst.

INTRODUCTION

Despite their discovery in the early 1930's in the heavy Hodonin crude of eastern Europe (1), adamantanes occasioned relatively little interest until a facile chemical synthesis was reported, in 1957 (2). Although notable as part of the diamondoids found in certain natural gas condensates (3, 4), adamantanes appear never to exceed about 0.02-0.04% in crudes (5), a concentration too low for economic recovery.

Unsubstituted adamantane was first prepared by the $AlCl_3$-catalyzed isomerization of hydrogenated cyclopentadiene dimer, tetrahydrodicyclopentadiene (THDCP), an approach which was quickly expanded to include a number of methyl adamantanes (6). Solid acid catalysts such as silica-alumina (7) and HY zeolite (8) were also able to effect the THDCP-adamantane transformation, but none was apparently competitive in yield and stability with $AlCl_3$ and/or $AlBr_3$.

In the present context, the most significant post-1960 advance in the synthesis of adamantanes was a change in feedstock, from THDCP to a variety of tricyclic perhydroaromatics (9). The effective catalyst was an AlX_3-HX-hydrocarbon mixture, where X = chloride or bromide. The products were methyl or polymethyl adamantanes, each having the same molecular weight as the feed tricycloalkane, often in a yield of some 60% or more. An example is shown in Figure 1. Subsequent work showed that numerous acid catalysts would convert tricyclic naphthenes (tricycloalkanes) into methyl adamantanes, namely, chlorinated Pt/Al_2O_3 (11), silica-alumina (12), silica-alumina with Group VIII metal (13), and REX/REY, usually with Group VIII metal (14).

Based on the chemical synthesis work, potential precursors to adamantanes exist in a crude in the form of high boiling polycyclic naphthenes and aromatics. In a modern refinery, these precursors, boiling above about 300°C, commonly encounter acid catalysts in both a fluid catalytic cracking (FCC) unit and in a hydrocracker (HDC). Thus, the present experiments focused on HDC recycle streams.

EXPERIMENTAL

Two zeolites were used in the experiments, Beta (15) and "ultrastable" Y (USY) (16). Framework SiO_2/Al_2O_3 ratios were approximately 50 for Beta and 200 for "ultra-stable" Y (USY). For better comparison with the USY, a sample of the Beta catalyst was dealuminated to a similar framework SiO_2/Al_2O_3 ratio and designated "low activity" Beta (LoAct-Beta). In the experiments, all catalysts contained alumina binder, all were 24/60 mesh, all contained 0.5% Pt or Pd, and all were brought to initial operating conditions (232°C and 2.5 mPa) in flowing hydrogen. The experiments were conducted in a downflow tubular reactor, at 2.5 mPa, with a H_2/hydrocarbon (H_2/HC) mole ratio of 3 - 4, at temperatures of 230° - 330°C, and at 1 - 4 WHSV (weight hourly space velocity). Day-to-day catalyst aging was not significant in these experiments.

Gas chromatography (gc) results were obtained with a 60m DB-1 capillary column (J&W Scientific, 0.25 mm id, 0.25µ film). The gc-mass spec analyses were performed on a Kratos Model MS80RFA, with a Hewlett Packard Series II 5890 gc and a 30m DB-5HT column (0.32 mm id, 0.1µ film). Ionization was by electron impact.

RESULTS AND DISCUSSION

Refinery streams selected for testing are shown in Table 1. Since most methyl and ethyl adamantanes boil between 180°C and 240°C, streams were selected to bracket that range, namely, a 135° - 210°C HDC heavy naphtha, a 175° - 375°C HDC recycle stream, a 175° - 260°C portion of the HDC recycle stream, and a 120° - 245°C hydrotreated kerosene, all from a refinery sourced largely with heavy crude. In addition, a 175° - 290°C analog of the above HDC recycle stream was obtained from a refinery sourced with light, conventional crude. Crude type was a consideration since, in general, heavy crudes are enriched in polycyclic alkanes relative to light, "conventional" crudes (17).

Isolation of adamantanes. The adamantanes shown in Figure 2a were obtained when the heavy crude HDC recycle stream described in Table 1 was passed over the Pt/LoAct-Beta catalyst at 325°C and 1.2 WHSV. Approximately 90% of the feed, which boiled above 175°C, was converted to lower boiling, mostly gasoline-range hydrocarbon. The remaining high-boiling material contained over 70% adamantane and methyl adamantanes. Gas chromatography (gc) and gc-mass spec showed the presence of diamantanes as well.

Comparison of Figures 2a and 2b showed the striking similarity between this potential refinery product and a mixture of naturally occurring adamantanes recovered from a deep gas condensate (4). Despite the understandable difference in carbon-number and isomer distribution, every major peak in the product from Pt/LoAct-Beta corresponded to a peak in the condensate adamantanes. Gc-mass spec confirmed the molecular weights indicated in Figure 2.

Adamantanes free from diamantanes were obtained by using a lower boiling portion of the HDC recycle stream. When the above experiments were repeated with a 175° - 260°C fraction of the HDC stream, this time using the high-activity Pt/Beta (50 SiO_2/Al_2O_3 ratio) at 260°C and 2.0 WHSV, conversion to lighter hydrocarbon was 86%. The product "mixed methyl adamantanes" (MMA's) were virtually indistinguishable from those obtained with full-range HDC recycle, and material boiling higher than the MMA's (e.g., diamantanes) was < 0.1% of the product.

MMA yield was substantial. With the 175° - 260°C feed, 9.1 g of MMA was obtained from 100 g of feed, representing 32% of the 3RN's. A second experiment, under slightly milder conditions, yielded 9.3 g of MMA, or 33%. The product MMA, separated from lower boiling hydrocarbons by distillation, was a colorless liquid with a density of 0.89 g/cc.

That the MMA's were associated with the recycle stream was further affirmed by a "blank" experiment with Pt/Beta and the 135° - 210°C HDC heavy naphtha, at 255°C and 1.9 WHSV.   The product containing only 0.6% MMA's, essentially all of which were bridgehead-methyl isomers boiling between 180° and 200°C.

Yield of adamantanes was much lower in a refinery operating on light, conventional crude. When a 1:1 blend of the light crude HDC recycle and the HDC heavy naphtha in Table 1 was processed over high-activity Pt/Beta, the product contained only 0.9 % MMA's.

A final experiment was conducted to probe for adamantanes in the crude supply to the heavy crude refinery. The feed was the hydrotreated kerosene, a stream which had never contacted a zeolite catalyst but which, given its 120° - 245°C boiling range, should contain any MMA's in the crude. As shown in Table 1, it analyzed 0.6% 3RN's. When processed over both Pd/Beta and Pt/Beta, the products contained 0.4% MMA's. This result strongly suggests that, while some portion of adamantanes did enter the refinery with the crude, the bulk was being formed, either in the HDC (and possibly FCC) unit or in these noble metal/zeolite experiments.

Formation of adamantanes. A model compound was used to probe possible formation of adamantanes over Pt and Pd/Beta catalysts under the conditions of these experiments. Based on the adamantane literature and on commercial

availability, perhydrofluorene (PHF) was the selected for most of the experiments. Boiling at 253°C, it should convert to 1,3,5-TriMA, as depicted in Figure 1.

The PHF to 1,3,5-TriMA conversion process was largely absent over zeolite Beta, for reasons which will be discussed below. Dissolved at 10% in HDC heavy naphtha and processed over high-activity Pt/Beta at 265°C and 1.6 WHSV, the yield of MMA's based on PHF was less than 5%. (PHF was 100% converted.) The very small amount of new MMA's in the product had methyl or ethyl groups on non-bridgehead carbons, and little or none of the "end" product, 1,3,5-TriMA, was formed. A similarly low MMA yield was obtained with phenanthrene, a molecule which might be expected to hydrogenate and isomerize to 1,3,5,7-TetMA over a noble metal/zeolite catalyst.

Choice of zeolite. Beta was selected for the first experiments because it is a member of a class called "large-pore" zeolites (18), a class which includes zeolite Y. The Beta pores, like those of Y, are formed from 12-membered rings of linked silicon and aluminum oxide tetrahedra. The opening of those pores in Beta is an elliptical 6.4· x 7.6 Å, while those of Y are a circular 7.4 Å (19). Unsubstituted adamantane, a spherical molecule with a Van der Waals diameter of 7.4 Å, is known to penetrate the pores of zeolite Y (8), but should have difficulty penetrating Beta, whose critical pore dimension is only 6.4 Å. Thus Beta was the zeolite of choice for isolating adamantanes. It is noteworthy, with respect to this approach to adamantanes, that MMA's had been isolated earlier by hydrocracking narrow-boiling, laboratory crude extracts over 10% Pt-on-diatomite, at temperatures of about 430°C (20).

Zeolite Y, while also effective in isolating adamantanes, was much more effective than Beta in generating them, as shown by experiments with PHF. When the PHF experiment described earlier was repeated over Pd/Y at 590°C and 1.7 WHSV, the product contained 3.5% MMA's which, when corrected for the heavy naphtha contribution, represented an approximately 27% yield based on PHF. Gc-mass spec showed four new non-bridgehead products, all C13 MMA's, and 1,3,5-TriMA was enhanced in concentration relative to the other bridgehead isomers. PHF, a C13 molecule, was 100% converted.

The PHF experiments demonstrated size-selective differentiation between zeolites Y and Beta, and they strongly suggested that some portion of the adamantanes isolated from these refinery streams were formed in the HDC unit and were only being concentrated in the experiments with Pt and Pd/Beta.

Higher severe experiments with Pd/Beta further demonstrated the size-discriminating ability of this zeolite. When the contact time between HDC heavy naphtha and Pd/Beta was increased, the smallest of the MMA's were converted, namely, unsubstituted adamantane and 1-MA. The larger MMA's presumably could not enter the pores of zeolite Beta and were essentially unconverted. With Pd/Y, at the same HDC heavy naphtha conversion levels, the relative reactivity relationships were reversed. The larger MMA's were preferentially converted.

CONCLUSIONS

These results show that adamantanes, while present in crudes, can both be formed and concentrated in certain refinery operations, most notably in an HDC unit, and that their amount depends on crude source, catalyst, refinery configuration, and operating conditions. A level of some 10% adamantanes is not unexpected in the 175° - 260°C portion of the HDC recycle stream in a refinery sourced by heavy crude. These adamantanes can be isolated very effectively from such streams by mild hydrocracking over large-pore zeolite catalysts, such as zeolite Beta.

ACKNOWLEDGEMENTS

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Table 1.

Boiling ranges and three-ring naphthene (3RN) contents of refinery streams tested for adamantanes.

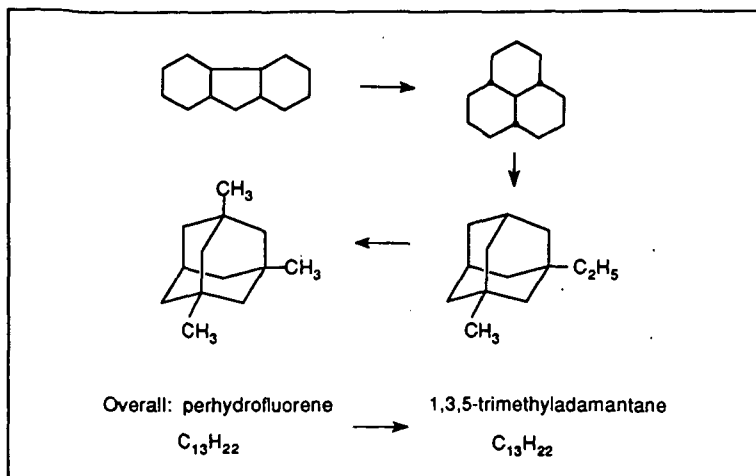| Stream	Boiling Range, °C	3RN *
Heavy crude HDC recycle stream	175 - 375	24
Fraction boiling below 260° (46 %)	175 - 260	28
Heavy crude HDC heavy naphtha	135 - 210	1.2
Heavy crude hydrotreated kerosene	120 - 245	0.6
Light crude HDC recycle stream	175 - 290	3.4

* By mass spectrometry

Figure 1. A simplified reaction scheme for the preparation of 1,3,5-trimethyladamantane from perhydrofluorene (10).
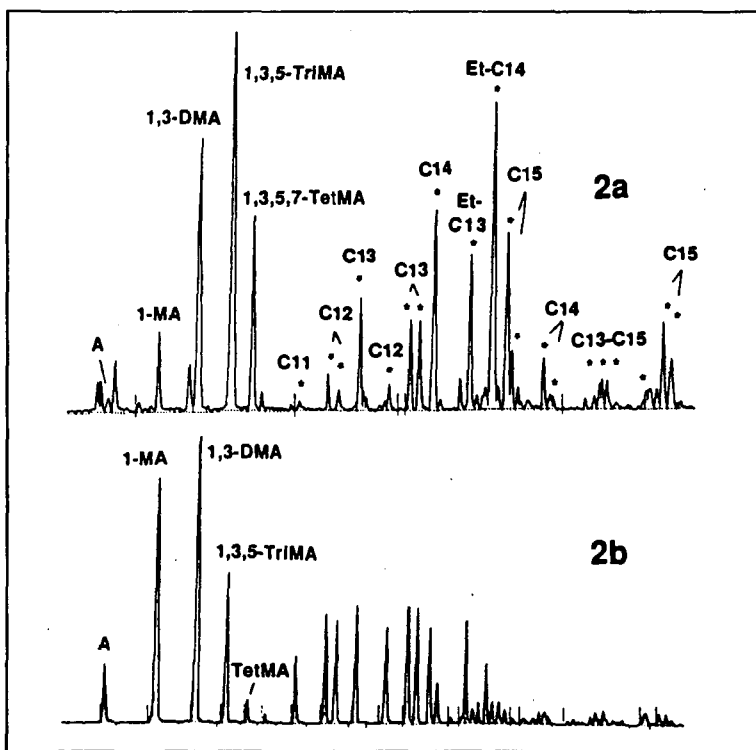

Figure 2. (a) Gc trace showing adamantanes isolated from 175° - 375°C heavy crude HDC recycle by processing over Pt/Beta. (b) Adamantanes recovered from a deep gas condensate. Asterisks in 2a indicate peaks which match those in 2b and which have MMA molecular weights by gc-mass spec.